



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**03.11.2004 Bulletin 2004/45**

(51) Int Cl.7: **H01G 9/20, H01L 51/20**

(21) Application number: **03405306.6**

(22) Date of filing: **30.04.2003**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR**  
**HU IE IT LI LU MC NL PT RO SE SI SK TR**  
 Designated Extension States:  
**AL LT LV MK**

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(54) **Dye sensitized solar cell**

(57) A dye sensitized solar cell, wherein the dye is an amphiphilic ruthenium polypyridil complex and wherein a stabilizing compound whose molecular struc-

ture comprises a hydrophobic part and an anchoring group, for example decylphosphonic acid (DPA), is co-adsorbed together with the dye on the semi-conductive metal oxide layer of the photoanode.

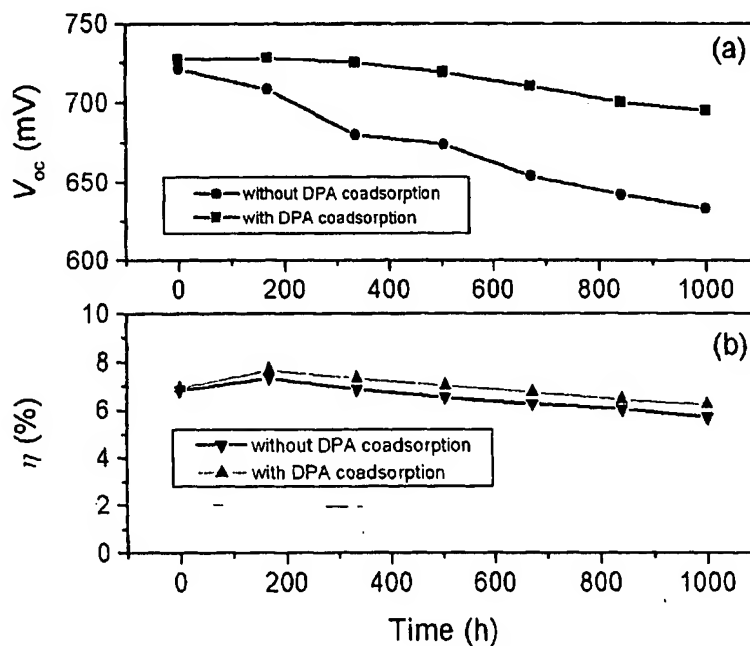


Figure 5

## Description

**[0001]** The present invention concerns a dye-sensitized solar cell or DSSC. DSSCs are regenerative photo-electrochemical cells comprising a photoanode, said photoanode comprising at least one semiconductive metal oxide layer on a conductive substrate, sensitized by at least one chromophoric substance, wherein said chromophoric substance is a ruthenium, osmium or iron complex with ligands selected from bidentate, tridentate and polydentate polypyridil compounds and at least one anchoring group, a counter-electrode, at least one of these electrodes being transparent or translucent, and an electrolyte positioned between these electrodes, the said electrolyte including a redox system, said redox system comprising an electrochemically active salt and a first compound forming a redox couple with either the anion or the cation of said electrochemically active salt.

**[0002]** In cells of this type, the said semi-conductive metal oxide layer is conveniently polycrystalline. For this purpose, particularly suitable are oxides of transition metals and elements either of the third main group, or of the fourth, fifth and sixth sub-groups of periodic table of elements. The use of nanocrystalline titanium dioxide was shown to be particularly advantageous, the surface of the photoanode in contact with the electrolyte being porous, with a porosity factor of preferably at least 20.

**[0003]** The term "nanocrystalline" means that the semiconductive metal oxide, in particular  $\text{TiO}_2$ , is in polycrystalline form with a granulometry of the order of several nanometers, for example 10 to 50 nanometers.

**[0004]** The "porosity factor" is defined as the ratio of the photo-electrochemically active surface of the photoanode to the surface area of the substrate covered by the layer(s) of semi-conductive metal oxide.

**[0005]** In this type of cell, a chromophoric substance, often called photosensitizer or photosensitizing dye, preferably forms a substantially monomolecular layer attached to the  $\text{TiO}_2$  layer by means of anchoring groups like carboxylate or phosphonate or cyano groups or chelating groups with  $\pi$ -conducting character like oxymes, dioxyms, hydroxyquinolines, salicylates and  $\alpha$ -keto-enolates. Several transition metal complexes, in particular ruthenium complexes with heterocyclic ligands like bidentate, tridentate or polydentate polypyridil compounds, have been shown to be efficient photosensitizing dyes. Cells of this type are already known and are described inter alia in EP 0333641 and EP 0525070.

**[0006]** Suitable electrolytes are those including a redox system consisting of a mixture of at least one electrochemically active salt and at least one molecule designed to form an oxidation-reduction system with the anion or cation of the said salt. Electrolytes wherein said electrochemically active salt has a melting point below ambient temperature or forms with the afore-said molecule a phase with a melting point below ambient temperature have been described in EP 0737358.

**[0007]** Dye-sensitized solar cells provide an economically credible alternative to conventional inorganic photovoltaic devices. Owing to their high-energy conversion efficiency and low production cost, they have received considerable attention over the past decade. The mesoscopic texture of the  $\text{TiO}_2$  film in these cells significantly increases the cross section of light harvesting by surface-anchored charge transfer sensitizers while maintaining a good contact with electrolytes. In these photovoltaic devices, ultrafast electron-injection from a photoexcited dye into the conduction band of an oxide semiconductor, and subsequently dye regeneration and hole transportation to the counter electrode, are responsible for the efficient generation of electricity. Although a respectable 10.4 % light-to-electricity conversion efficiency at AM 1.5 solar irradiance has been obtained for photovoltaic devices with a panchromatic dye and a liquid electrolyte containing the triiodide/iodide couple, as reported in J. Am. Chem. Soc. 123, 1613-1624 (2001), the achievement of long-term stability at temperatures of 80~85°C, which is an important requirement for outdoor application of the DSSC, still remains a major challenge.

**[0008]** The leakage of liquid electrolyte from such DSSC modules, possible desorption of loosely attached dyes and photodegradation in the desorbed state, as well as corrosion of the photoelectrode and/or counter electrode by the triiodide/iodide couple, may be considered as some critical factors limiting the long-term performance of the DSSC, especially at elevated temperature. A particular problem of stability at 80°C in DSSCs containing the iodide/triiodide redox couple, upon aging, is the drop in open circuit potential (Voc), causing the poor stability. It is believed that the dark current of DSSCs increases and Voc decreases, due to the interaction of triiodide with bare zones of the  $\text{TiO}_2$  electrode, that is not completely covered with dye molecules. Efforts to realize devices with high efficiencies that meet the stability criteria for outdoor use may deal with new counter electrode materials, alternative redox couples and new sensitizers. Additionally, gelified materials incorporating triiodide/iodide as a redox couple, as disclosed by EP 1087412, were introduced to substitute the liquid electrolytes by quasi-solid state materials. Polymer gel electrolytes comprising a non-conducting polymer and an organic molten salt have been proposed by US 6,245,847, with special emphasis on applications to lithium batteries, super capacitors or electrochromic windows for mitigating the potential instability against leakage under thermal stress.

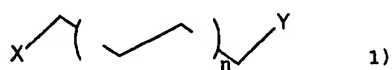
**[0009]** However, until now, few satisfactory long-term thermal stability results at temperatures up to 80°C are reported for high power DSSCs, together with acceptable efficiencies, and it is still necessary to propose measures, which alone or in combination, are capable to improve such thermostability of DSSCs.

**[0010]** According to a first aspect of the DSSC according to the present invention, a stabilizing compound is co-

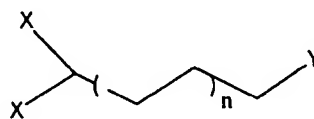
adsorbed with the dye on the surface of the semi-conductive metal oxide layer. The molecular structure of said stabilizing compound comprises a hydrophobic part and at least one anchoring functional group, selected from the group consisting of  $\text{COOH}$ ,  $\text{PO}_3\text{H}_2$ ,  $\text{PO}_4\text{H}_2$ ,  $\text{SO}_3\text{H}_2$ ,  $\text{SO}_4\text{H}_2$ , or deprotonated forms thereof. In particular, said stabilizing compound may be selected from the group of compounds having one of formulae 1 to 12:

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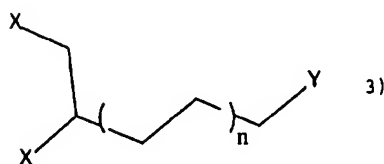


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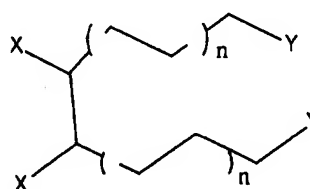


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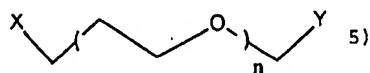


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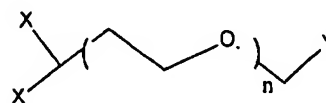


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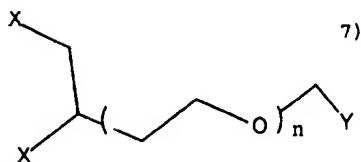


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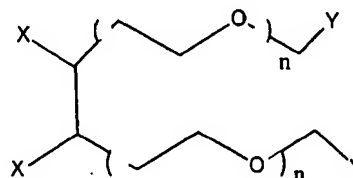


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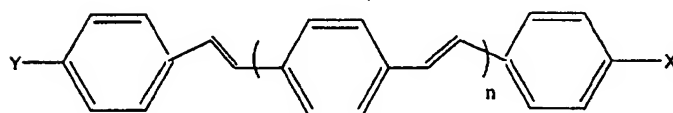
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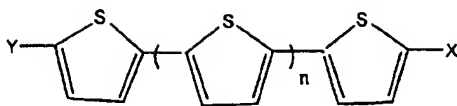
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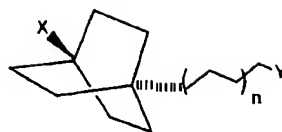
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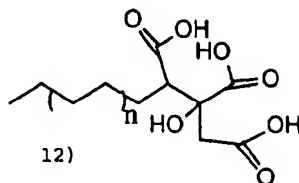
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10)



11)



12)

with  $n = 0$  to  $20$ ,  $x$  and  $y$  being independently one of the other  $\text{COOH}$ ,  $\text{PO}_3\text{H}_2$ ,  $\text{PO}_4\text{H}_2$ ,  $\text{SO}_3\text{H}_2$ ,  $\text{SO}_4\text{H}_2$ , or deprotonated forms thereof, with the proviso that  $x$  and  $y$  are not simultaneously  $\text{H}$ .

**[0011]** The stabilizing compound may be selected from the group consisting of alkyl carboxylic acids, alkyl dicarboxylic acids, alkyl carboxylates, alkyl phosphonic acids, alkyl phosphonates, alkyl diphosphonic acids, alkyl diphosphonates, alkyl sulphonic acids, alkyl sulphonates, wherein alkyl is linear or branched from  $\text{C}_1$  to  $\text{C}_{20}$ .

**[0012]** The stabilizing compound may be selected from cholic acid, deoxycholic acid, chenodeoxycholic acid, ursodeoxycholic acid, lithocholic acid, cyclohexane-carboxylic acid, adamantane acetic acid, adamantane propionic acid and 4-pentylbicyclo (2,2,2)-octane-1-carboxylic acid.

**[0013]** It is believed that said sensitizing dye and said stabilizing compound form a self-assembled packed monolayer on said semi-conductive metal oxide layer, wherein the molar ratio of said sensitizing dye to said co-adsorbed second compound may be of between 5 and 1.

**[0014]** Without being bound by theory, it is believed that the sensitizing dye molecules and the co-adsorbing molecules constitute a closed packed self-assembled monolayer forming a barrier versus triiodide. It is believed that the triiodide can no more reach the  $\text{TiO}_2$  surface and that therefore the dark current decreases by decreasing the back electron transfer from the photo injected electrons of  $\text{TiO}_2$  to triiodide. It is further believed that the presence of the co-adsorbing second compound contributes in structuring the arrangement of the adsorbed dye molecules.

**[0015]** According to a second aspect of the DSSC, object of the present invention, the sensitizing dye may be selected among ruthenium complexes having an amphiphilic structure. Amphiphilic structures are obtained by substituting hydrophobic substituents, in particular aliphatic chains of tuned length, on the heterocyclic ligands of Ru. Among suitable dyes are compounds of formula  $\text{RuLL}'\text{X}_2$ , wherein L is 4,4'-di-carboxylic acid, 2,2'-bipyridine and L' is 4,4'-di-alkyl-2,2'-bipyridine, wherein the alkyl substituent has a mid-sized chain length, in particular  $\text{C}_6$  -  $\text{C}_{20}$ , and X is a halogen,  $\text{H}_2\text{O}$ , CN and amine, NCS or NCO.

**[0016]** A particularly preferred sensitizing dye is Z-907, which is a Ru(II) complex of formula  $\text{RuLL}'(\text{NCS})_2$ , in which L represents the ligand 4,4'-dicarboxylate-2,2'-bipyridine and L' represents the ligand 4,4'-dinonyl-2,2'-bipyridine.

**[0017]** Without being bound by theory, it is believed that the hydrophobic part of the sensitizing dye, in particular a substituent alkyl chain of mid-sized length of between  $\text{C}_6$  -  $\text{C}_{20}$ , co-operating with the hydrophobic part of the afore-said second co-adsorbing compound, in particular an alkyl chain of appropriate length, forms a substantially dense hydrophobic layer shielding the surface of the semi-conductive metal oxide layer. In turn, when the molecules co-adsorbed with the sensitizing dye have a sufficient chain length and if the free ends of these chains bear an acidic group (Y), these groups surmount the hydrophobic layer and are capable to repelling with species present in the electrolyte, thereby preventing once again direct interaction of the species of the electrolyte with parts of the semi-conductive metal oxide surface itself.

**[0018]** According to another aspect of the DSSC, object of the present invention, the electrolyte of the DSSC may comprise a polar organic solvent having a high boiling point. Boiling points over  $100^\circ\text{C}$  at standard atmospheric pressure are preferred. A suitable compound to be used as organic solvent in the framework of the present invention may be found among nitriles. A preferred nitrile is 3-methoxypropionitrile (MPN).

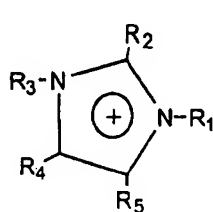
**[0019]** The solvent may be useful on one hand for solubilizing an electrochemically active salt, which shall be present in the electrolyte, and/or the said first compound forming the redox couple with an ion of said salt. On the other hand, a solvent with a relatively low boiling point may be useful to dissolve the matrix polymer during the manufacturing process of the cell, a part of said solvent being removed, for example by suction under vacuum, upon completion of said process. The solvent which may amount to 1 - 20 % by weight of the electrolyte may also act as a plasticizer on

the matrix polymer.

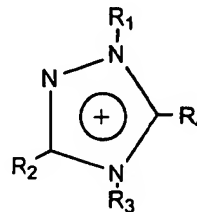
[0020] According to a further aspect of the DSSC, object of the present invention, the electrolyte of the DSSC may comprise a gelifying compound, in particular a polymer forming a polymer matrix. A polymer matrix provides a beneficial physical state to the electrolyte, namely a solid state, a quasi-solid state, a rubber-like state or a gel state, depending on the composition which is maintained at the operating temperature of the cell under adverse conditions, namely at least up to 80°C. A suitable polymer may be selected from polyvinylidene fluoride (PVDF), polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), polyvinylidene fluoride-chlorotrifluoroethylene (PVDF-HFP-CTFE) copolymers, polyethylene oxide, polymethylmethacrylate, polyacrylonitrile, polypropylene, polystyrene, polybutadiene, polyethyleneglycol, polyvinylpyrrolidone, polyaniline, polypyrrole, polythiophene and their derivatives. Preferred polymers are polyvinylidene fluoride-hexafluoropropylene copolymers (PVDF-HFP).

[0021] The electrolyte of the DSSC object of the present invention may also comprise, as a gelifying compound, a metal oxide in form of nanoparticles capable to form a gel matrix. Such gel matrix provides a beneficial physical state to the electrolyte, namely a solid state, a quasi-solid state or a gel state, that is maintained at the operating temperature of the cell under adverse conditions, namely at least up to 80°C. A suitable nanoparticle metal oxide may be selected from SiO<sub>2</sub> or TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, or MgO or TiO<sub>2</sub> nano-tubes or TiO<sub>2</sub> nano-rods, wherein the gel contains said nanoparticles in minor proportions, preferably ≤ 10 Wt %. Preferred gelifying compounds are SiO<sub>2</sub> or TiO<sub>2</sub> nanoparticles, which may amount to 2 - 20 Wt % of the electrolyte.

[0022] In still another aspect of the DSSC according to the present invention, the electrolyte may comprise, instead of an electrochemically active salt which is solid at ambient temperature and shall be dissolved in a solvent, a so-called "room temperature molten salt", an electrochemically active salt having a melting point lower than ambient temperature, or a salt selected so that the mixture formed by this salt and another species of the redox system has a melting point lower than ambient temperature. Then, presence of a solvent may be avoided. The cation of the electrochemically active salt may comprise at least one quaternary nitrogen. The quaternary nitrogen may be comprised in a group selected from imidazolium and triazolium type groups, corresponding to the following general formulae (a) or (b):



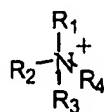
(a)



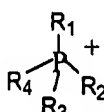
(b)

where the groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are identical or different and are selected from hydrogen and linear or branched alkyl groups, with 1 to 20 carbon atoms, linear or branched alkoxy groups with 1 to 20 atoms of carbon, fluoride substitution derivatives of alkyl groups, alkenyl groups, and combinations of these groups and the corresponding halogenides, or from the alkoxyalkyl and polyether groups.

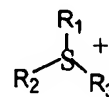
[0023] The cation of the electrochemically active salt may also be an ammonium, a phosphonium or a sulfonium group corresponding to the following general formulae (c), (d) or (e):



(c)



(d)



(e)

[0024] In which groups R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> have the same meanings as above.

[0025] The anion of said ionic liquid salt may be selected from halide ions, or a polyhalide ion, or a complex anion containing at least one halide ion, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, or CF<sub>3</sub>COO<sup>-</sup> or (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>C<sup>-</sup> or NO<sub>3</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup> or N(CN)<sub>2</sub><sup>-</sup> or NCS<sup>-</sup> or R SO<sub>3</sub><sup>-</sup> or RSO<sub>4</sub><sup>-</sup>, where R is selected from hydrogen and linear or branched alkyl groups, with 1 to 20

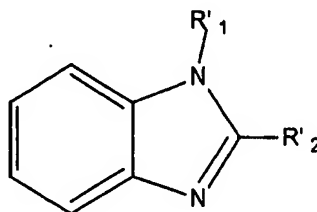
carbon atoms, linear, or branched alkoxy groups with 1 to 20 atoms of carbon.

[0026] The redox system of the electrolyte may comprise two salts or more, each having a melting point below ambient temperature, the anions forming a couple of two different electrolytes, for example the iodide/bromide couple.

[0027] In a still further aspect of the DSSC, object of the present invention, the electrolyte incorporates a first compound co-operating with either the anion or the cation of the electrochemically active salt, that is to say forming a redox couple with said ion. As a well-known example of such a couple, if the anion of the electrochemically salt is I<sup>-</sup>, the neutral molecule, respectively element, is iodine.

[0028] In still a further aspect of the DSSC, object of the present invention, the electrolyte may incorporate a stabilizing additive in form of a neutral molecule comprising one or more nitrogen atom(s) with a lone electron pair.

[0029] Said neutral molecule may be selected from molecules having following formula:



wherein R'<sub>1</sub> and R'<sub>2</sub> can be H, alkyl, alkoxy, alkenyl, alkynyl, alkoxy-alkyl, poly-ether, and/or phenyl, independently one from the other, the number of carbon atoms of each substituent ranging from 1 to 20, the substitute being linear or branched.

[0030] Preferred compounds are Benzimidazole, 1-methylbenzimidazole, 1-methyl-2-phenyl benzimidazole and 1,2-dimethyl benzimidazole.

[0031] The presence of the afore-said neutral additive compound in the electrolyte increases the stability of the DSSC.

[0032] Other particulars and advantages of the DSSC according to the invention, in particular improved performance and stability, will appear to those skilled in the art from the description of a preferred embodiment as follows.

#### Fabrication of solar cells

[0033] The dye Z-907 is synthesized according to the method described in Langmuir 2002, 18, 952-954.

[0034] A screen-printed double layer of TiO<sub>2</sub> particles was used as photoanode. A 10 μm thick film of 20 nm sized TiO<sub>2</sub> particles was first printed on the fluorine-doped SnO<sub>2</sub> conducting glass electrode and further coated by 4 μm thick second layer of 400 nm light scattering anatase particles (CCIC, Japan). After sintering at 500°C and cooling down to 80°C, the TiO<sub>2</sub> electrodes were dye-coated by immersing them into a 0.3 mmol·l<sup>-1</sup> solution of Z-907 in acetonitrile and tert-butanol (volume ratio: 1:1) at room temperature for 12 hours and then assembled with thermally platinized conducting glass electrodes.

[0035] Self-assembled monolayers combining dye and co-adsorbent compound 1-decylphosphonic acid were obtained by dissolving in the same solvent as above Z-907 and the co-adsorbent compound in a molar ratio 4:1. Depending upon the selection of the dye and the co-adsorbent, i.e. their relative affinity constant for the TiO<sub>2</sub> layer, the ratio of dye and co-adsorbent can be varied from 1:10 to 10:1. After overnight soaking, the electrode was washed with acetonitrile to remove loosely bound dye and/or co-adsorbent molecules. The following construction steps of the solar cells photoelectrodes having neat Z-907 adsorbed on the TiO<sub>2</sub> layer and combined Z-907 + co-adsorbent on the TiO<sub>2</sub> layer are the same.

[0036] The electrodes were separated by a 35 μm thick hot-melt ring (Bynel, DuPont) and sealed up by heating. PVDF-HFP (5 wt %) was mixed with the liquid electrolyte consisting of DMPH (1,2 dimethyl-3-propylimidazolium iodide 0.6 mol l<sup>-1</sup>), iodine (0.1 mol l<sup>-1</sup>), NMBI (N-methylbenzimidazole 0.5 mol l<sup>-1</sup>) in MPN (3-methoxypropionitrile) and heated until no solid was observed. The internal space of the cell was filled with the resulting hot solution using a vacuum pump. After cooling down to room temperature, a uniform motionless polymer gel layer was formed in cells. The electrolyte-injecting hole made with a sand-ejecting drill on the counter electrode glass substrate was sealed with a Bynel sheet and a thin glass cover by heating. In order to have a good comparison with the polymer gel electrolyte, devices with the liquid electrolyte were also fabricated using the above procedure.

[0037] Fig. 1 presents a typical photocurrent density-voltage curve for cells based on the Z-907 dye and the polymer gel electrolyte under AM 1.5 sunlight illumination. The short-circuit photocurrent density (J<sub>sc</sub>), open-circuit voltage (V<sub>oc</sub>), and fill factor (FF) are 12.5 mA cm<sup>-2</sup>, 730 mV and 0.67, respectively, yielding an overall energy conversion efficiency (η) of 6.1 %. The action spectrum of the photocurrent is shown in the inset of Fig. 1. The incident photon-to-

current conversion efficiency (IPCE) reaches a maximum efficiency of 80 % at 540 nm. The photovoltaic performance obtained with liquid and polymer gel electrolytes is almost identical (Table 1) indicating that gelation has no adverse effect on the conversion efficiency.

[0038] Fig. 2 presents the detailed behaviour of device parameters during the aging tests performed at 80°C with the DSC containing polymer gel electrolyte. After the first week of aging the efficiency was moderately enhanced due to an increase in the Jsc and FF values. Then a gradually small decrease in the Voc without much variation in Jsc and FF caused a decrease in the overall efficiency by 6 %. This is well within the limit of thermal degradation accepted for silicon solar cells.

[0039] The device also showed an excellent photostability when submitted to accelerated testing in a solar simulator at 100 mW cm<sup>-2</sup> intensity. Thus after 1,000 h of light soaking at 55°C the efficiency had dropped by less than 5 % (figure 3b) for cells covered with a UV absorbing polymer film. The efficiency difference for devices tested with and without the polymer film was only 4 % at AM 1.5 sunlight indicating a very small sacrifice in efficiency due to UV filter.

[0040] The high conversion efficiency of the cell was sustained even under heating for 1,000 h at 80 °C, maintaining 94 % of its initial value after this time period as shown in figure 2. The device using the liquid electrolyte retained only 88 % of its initial performance under the same condition. The difference may arise from a decrease in solvent permeation across the sealant in the case of the polymer gel electrolyte. The polymer gel electrolyte is quasi-solid at room temperature but becomes a viscous liquid (viscosity: 4.34 mPa.s) at 80°C compared with the blank liquid electrolyte (viscosity: 0.91 mPa.s). Tolerance of such a severe thermal stress by a DSC having over 6 % efficiency is unprecedented. Whereas in the case of the N-719 dye RuL<sub>2</sub> (NCS)<sub>2</sub> the overall efficiency decreased almost 35 % during the first week at 80°C, figure 3a clearly reflects the effect of molecular structure of the sensitizer on the stability of the DSSC. The difference between N-719 and Z-907 is that one of the L ligands 4,4'-dicarboxylic acid-2, 2'-bipyridine is replaced with 4,4'-dinonyl-2, 2'-bipyridine to make the dye more hydrophobic. We believe that desorption of N-719 at high temperature resulted in the poor thermostability of related devices. So far, dye sensitised solar cells have been plagued by performance degradation at temperatures between 80 and 85°C. The best result obtained in previous studies was a decline in conversion efficiency from initially 4.5 to 3 % when the cell was maintained over 875 h at 85°C. The use of the amphiphilic Z-907 dye in conjunction with the polymer gel electrolyte was found to result in remarkably stable device performance both under thermal stress and light soaking.

[0041] Self-assembled monolayers combining dye and co-adsorbent compound hexadecylmalonic acid (HDMA) were obtained by dissolving in the same solvent as above Z-907 and the co-adsorbent compound in a molar ratio 1:1. After overnight soaking, the electrode was washed with acetonitrile to remove loosely bound dye and/or co-adsorbent molecules. The following construction steps of the solar cells photoelectrodes having neat Z-907 adsorbed on the TiO<sub>2</sub> layer and combined Z-907 + co-adsorbent on the TiO<sub>2</sub> layer are the same.

[0042] The electrodes were separated by a 35 µm thick hot melt ring (Bynel, DuPont) and sealed up by heating. The liquid electrolyte consisting of MP11 (1 methyl-3-propylimidazolium iodide 0.6 mol l<sup>-1</sup>), iodine (0.1 mol l<sup>-1</sup>), NMBI (N-methylbenzimidazole 0.5 mol l<sup>-1</sup>) in MPN (3-methoxypropionitrile) injected into the cell. As shown in Figure 4 the overall cell efficiency with same electrolyte increases in presence of HDMA co-adsorbent from 7.2 to 7.9 due to the increase in the open circuit potential (Voc) and current density. The device efficiencies at different light intensities is reported in Table 2. It clearly shows the enhancement of efficiencies due to the co-adsorption of HDMA with Z-907 dye.

[0043] Self-assembled monolayers combining dye and co-adsorbent compound 1-decylphosphonic acid (DPA) were obtained by dissolving in the same solvent as above Z-907 and the co-adsorbent compound in a molar ratio 4:1. After overnight soaking, the electrode was washed with acetonitrile to remove loosely bound dye and/or co-adsorbent molecules. The following construction steps of the solar cells photoelectrodes having neat Z-907 adsorbed on the TiO<sub>2</sub> layer and combined Z-907 + co-adsorbent on the TiO<sub>2</sub> layer are the same.

[0044] The electrodes were separated by a 35 µm thick hot melt ring (Bynel, DuPont) and sealed up by heating. The liquid electrolyte consisting of MP11 (1 methyl-3-propylimidazolium iodide 0.6 mol l<sup>-1</sup>), iodine (0.1 mol l<sup>-1</sup>), NMBI (N-methylbenzimidazole 0.5 mol l<sup>-1</sup>) in MPN (3-methoxypropionitrile) injected into the cell. As shown in figure 5a the drop in the Voc of device with co-adsorbent DPA significantly increases during the 1000 h aging of device at 80°C.

Table 1:

Device efficiencies of cells with the liquid and polymer gel electrolytes.				
Electrolytes	η (%) at different incident light intensities*			
	0.01 Sun	0.1 Sun	0.5 Sun	1.0 Sun
Liquid	7.5	7.4	6.9	6.2
Gel	7.6	7.3	6.8	6.1

\* The spectral distribution of the lamp mimics air mass 1.5 solar light. 1.0 Sun corresponds to an intensity of 100 mW cm<sup>-2</sup>.

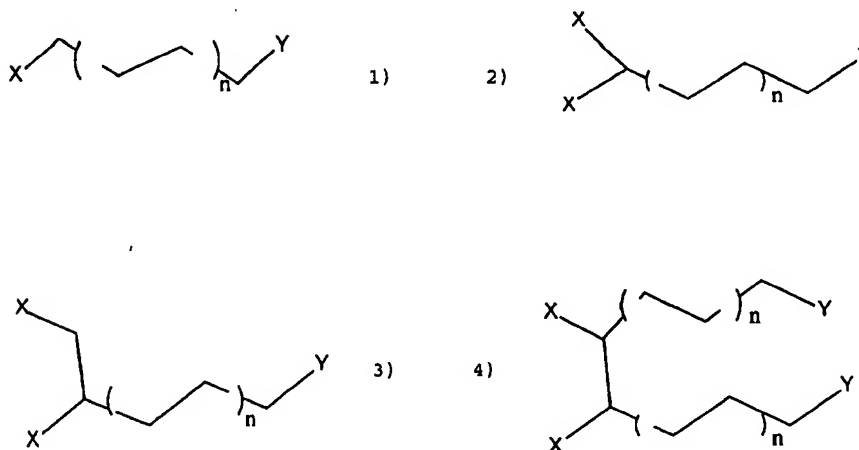
Table 2:

Device efficiencies of cells with the liquid electrolytes.				
Dye	$\eta$ (%) at different incident light intensities*			
	0.01 Sun	0.1 Sun	0.5 Sun	1.0 Sun
Z-907	7.2	7.6	7.7	7.2
Z-907 + HDMA	8.6	8.7	8.4	7.9

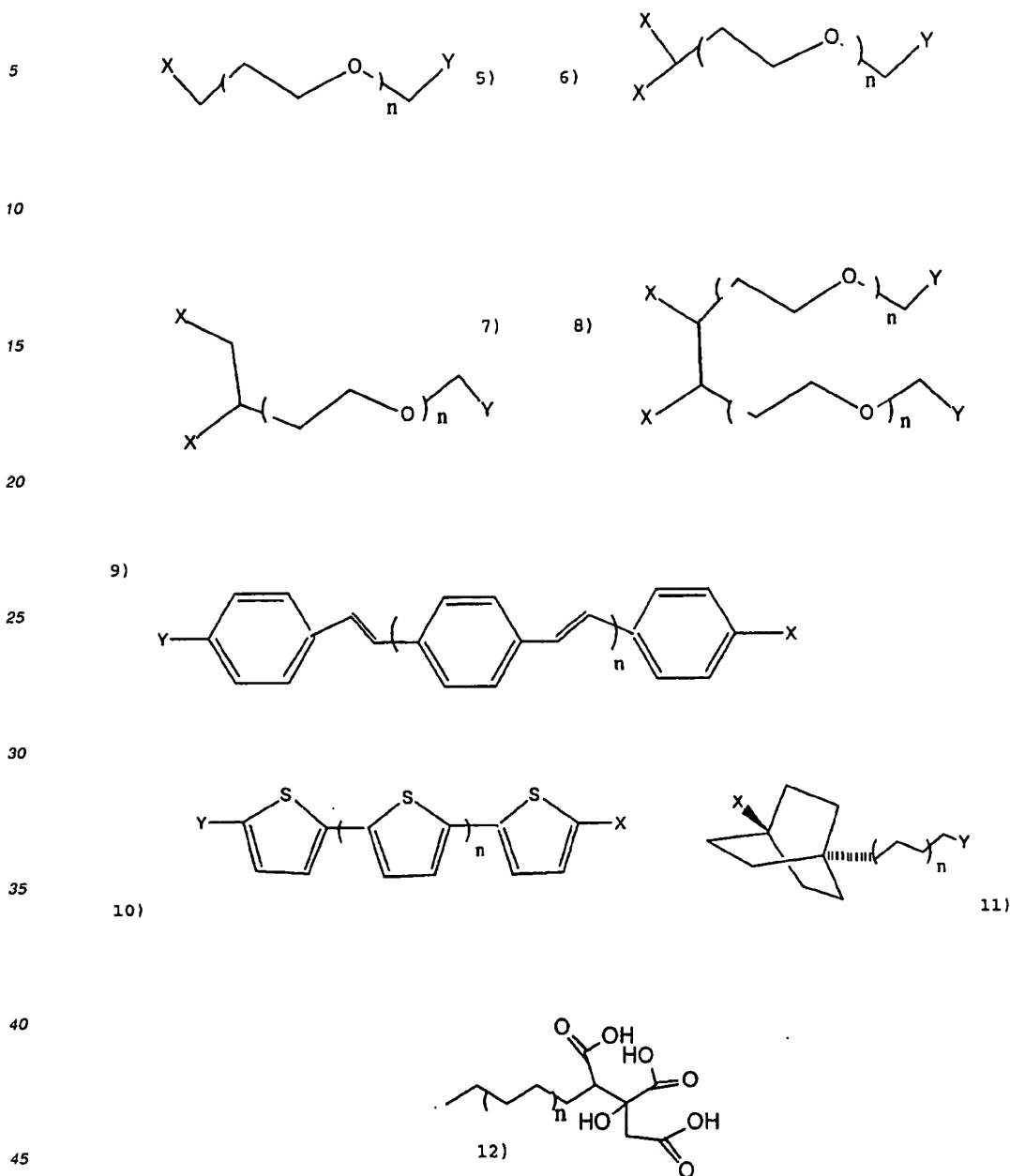
\* The spectral distribution of the lamp mimics air mass 1.5 solar light. 1.0 Sun corresponds to an intensity of  $100 \text{ mW cm}^{-2}$ .

### Claims

1. A regenerative photoelectrochemical cell comprising a photoanode, said photoanode comprising at least one semi-conductive metal oxide layer on a conductive substrate, sensitized by at least one chromophoric substance adsorbed on said semi-conductive metal oxide layer, wherein said chromophoric substance is a ruthenium, osmium or iron complex with ligands selected from bidentate, tridentate and polydentate polypyridil compounds and at least one anchoring group, a counter electrode, at least one of these electrodes being transparent or translucent, and an electrolyte arranged between said semi-conductive metal oxide layer and said counter electrode, said electrolyte comprising a redox system, said redox system comprising an electrochemically active salt and a first compound forming a redox couple with either the anion or the cation of said electrochemically active salt, **characterized in that** a second compound whose molecular structure comprises a hydrophobic part and at least one anchoring functional group, selected from the group consisting of  $\text{COOH}$ ,  $\text{PO}_3\text{H}_2$ ,  $\text{PO}_4\text{H}_2$ ,  $\text{SO}_3\text{H}_2$ ,  $\text{SO}_4\text{H}_2$ , and deprotonated forms thereof is co-adsorbed together with said chromophoric substance on said semi-conductive metal oxide layer.
2. A cell as claimed in claim 1, **characterized in that** said second compound is selected from the group of compounds having one of formulae 1 to 12:







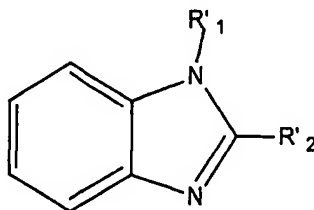
with  $n = 0$  to  $20$ ,  $x$  and  $y$  being, independently one of the other,  $\text{COOH}$ ,  $\text{PO}_3\text{H}_2$ ,  $\text{PO}_4\text{H}_2$ ,  $\text{SO}_3\text{H}_2$ ,  $\text{SO}_4\text{H}_2$ , or deprotonated forms thereof, with the proviso that  $x$  and  $y$  are not simultaneously  $\text{H}$ .

3. A cell as claimed in claim 1, **characterized in that** said second compound is selected from the group consisting of alkyl carboxylic acids, alkyl dicarboxylic acids, alkyl carboxylates, alkyl phosphonic acids, alkyl phosphonates, alkyl diphosphonic acids, alkyl diphosphonates, alkyl sulphonic acids, alkyl sulphonates, wherein alkyl is linear or branched from  $\text{C}_1$  to  $\text{C}_{20}$ .

4. A cell as claimed in claim 1, **characterized in that** said second compound is selected from cholic acid, deoxycholic acid, chenodeoxycholic acid, ursodeoxycholic acid, lithocholic acid, cyclohexane-carboxylic acid, adamantane

acetic acid, adamantane propionic acid and 4-pentylbicyclo(2,2,2)-octane-1-carboxylic acid.

- 5 5. A cell as claimed in anyone of claims 1 to 4, **characterized in that** said chromophoric substance and said second compound form a self-assembled monolayer on said semi-conductive metal oxide layer, wherein the molar ratio of said chromophoric substance to said co-adsorbed second compound is of between 5 and 1.
6. A cell according to anyone of the preceding claims, **characterized in that** said chromophoric substance is an amphiphilic ruthenium polypyridil complex.
- 10 7. A cell as claimed in anyone of the preceding claims, **characterised in that** said chromophoric substance is a Ru (II) complex of formula  $RuLL'(NCS)_2$ , in which L represents the ligand 4,4'-dicarboxylate-2,2'-bipyridine and L' represents the ligand 4,4'-nonyl-2,2'-bipyridine.
- 15 8. A cell as claimed in anyone of the preceding claims, **characterized in that** said electrolyte comprises an effective gelifying amount of a gelifying compound.
9. A cell as claimed in claim 8, **characterized in that** said gelifying compound is a matrix forming polymer.
- 20 10. A cell as claimed in claim 9, **characterized in that** said polymer is selected from the group consisting of polyvinylidenefluoride (PVDF), polyvinylidenehexafluoropropylene (PVD-HFP), polyvinylidenehexafluoropropylene-chlorotrifluoroethylene (PVD+HFP+CTFE) copolymers, polyethylene oxide, polymethylmethacrylate, polyacrylonitrile, polypropylene, polystyrene, polybutadiene, polyethyleneglycol, polyvinylpyrrolidone, polyaniline, polypyrrole, polythiophene and derivatives thereof.
- 25 11. A cell as claimed in anyone of the preceding claims, **characterized in that** said electrolyte comprises a copolymer of polyvinylidenefluoride-hexafluoropropylene (PVDF-HFP) and **in that** the amount of said PVDF-HFP copolymer is of between 2 % and 50 % by weight of the electrolyte.
- 30 12. A cell as claimed in claim 8, **characterized in that** said gelifying compound is selected from the group consisting of  $SiO_2$ ,  $TiO_2$  and  $Al_2O_3$  nanoparticles, MgO and  $TiO_2$  nano-tubes,  $TiO_2$  nano-rods, wherein the gel contains said gelifying compound in minor proportions, of between 2 % and 20 % by weight of the electrolyte, in particular  $\leq 10$  Wt %.
- 35 13. A cell as claimed in anyone of the preceding claims, **characterized in that** said electrolyte comprises a room temperature molten salt, said molten salt being liquid at least between standard room temperature and 80°C above said room temperature.
- 40 14. A cell as claimed in anyone of the preceding claims, **characterized in that** said electrolyte further comprises a polar organic solvent having a boiling point of 100°C or greater than 100°C at normal atmospheric pressure.
- 45 15. A cell as claimed in claim 14, **characterized in that** said solvent is a nitrile selected from 3-methoxypropionitrile and butyronitrile.
16. A cell as claimed in anyone of the preceding claims, **characterized in that** said electrolyte further comprises, as an additive, a compound formed by a neutral molecule comprising one or more nitrogen atom(s) with a lone electron pair.
17. A cell as claimed in claim 16, **characterized in that** said neutral molecule has following formula:



wherein  $R'_1$  and  $R'_2$  can be H, alkyl, alkoxy, alkenyl, alkynyl, alkoxy-alkyl, poly-ether, and/or phenyl, independently one from the other, the number of carbon atoms of each substituent ranging from 1 to 20, the substitute being linear or branched.

- 5 18. A compound of formula  $RuLL'(NSC)_2$ , wherein L represents the ligand 4,4'-dicarboxylate-2,2'-bipyridine and L' represents the ligand 4,4'-dinonyl-2,2'-bipyridine.

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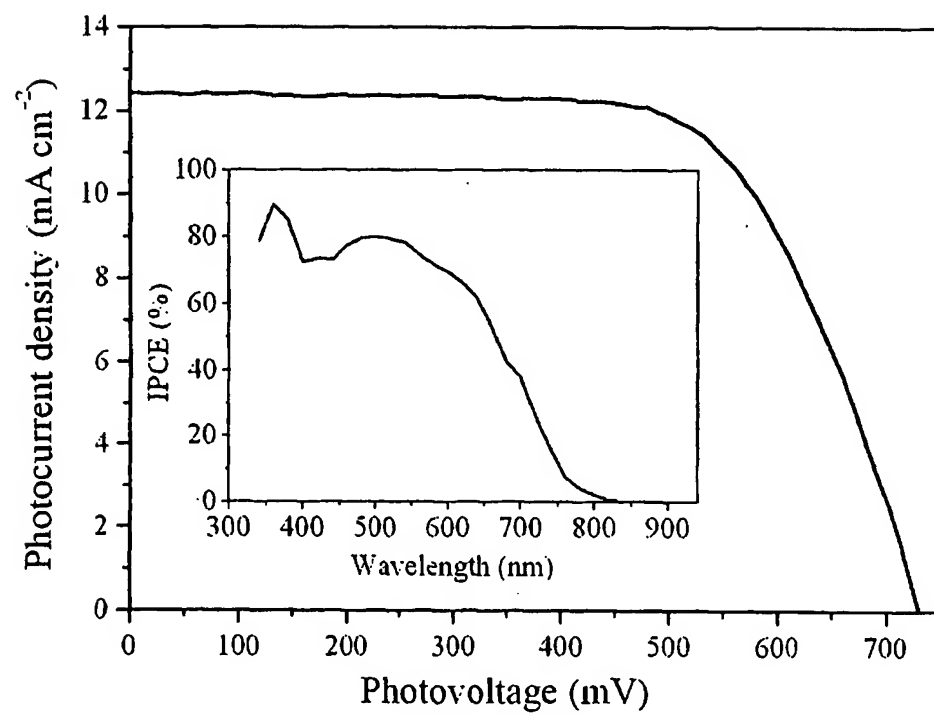


Figure 1

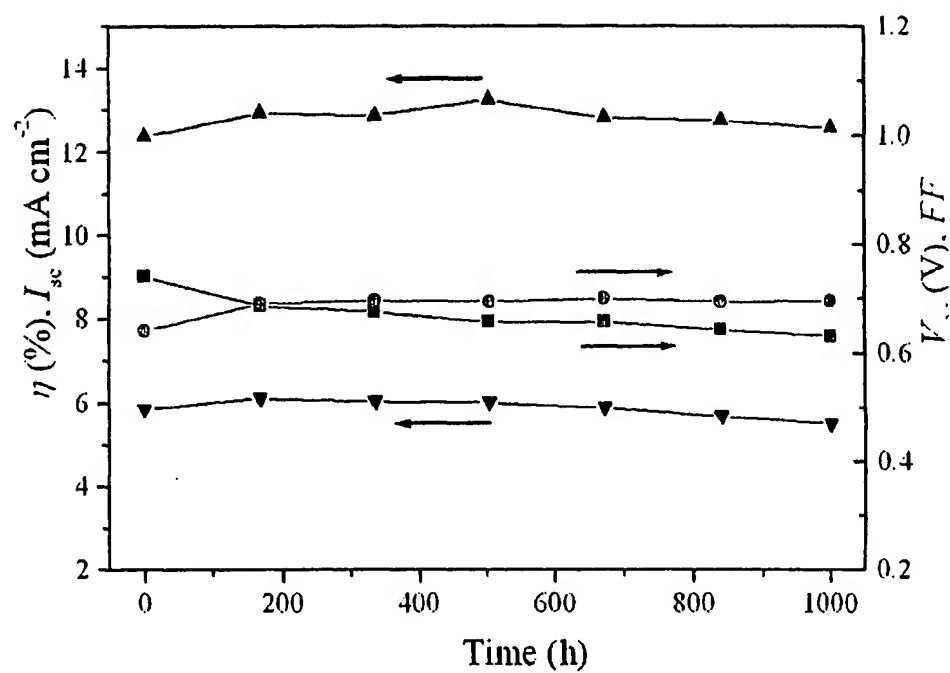


Figure 2

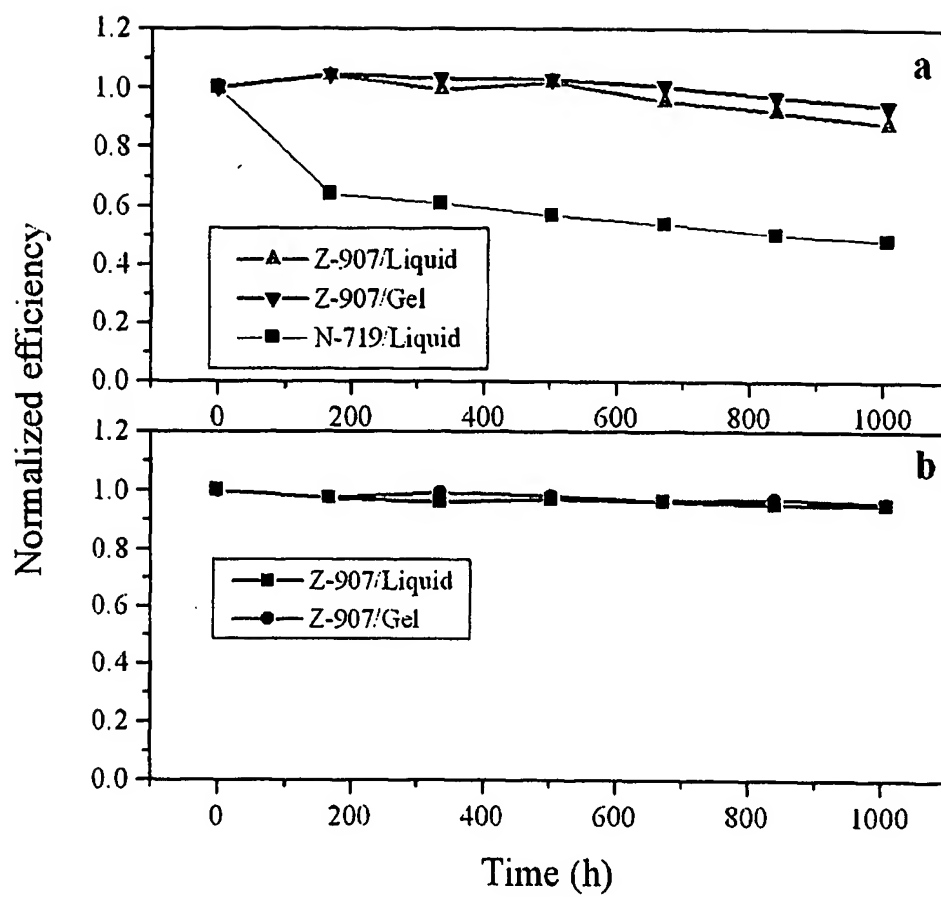


Figure 3

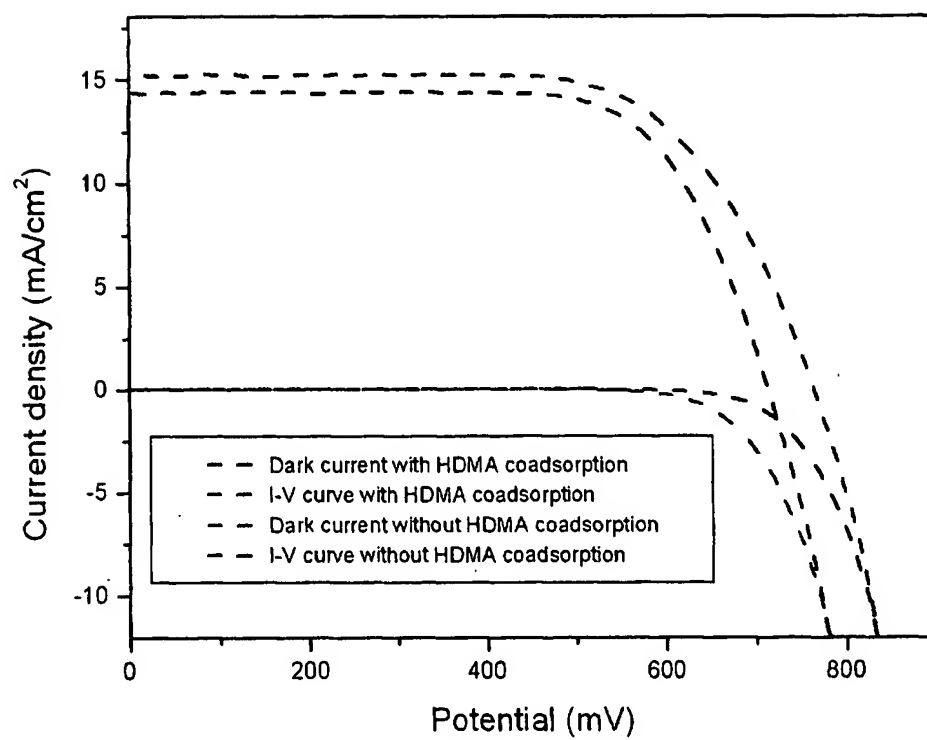


Figure 4

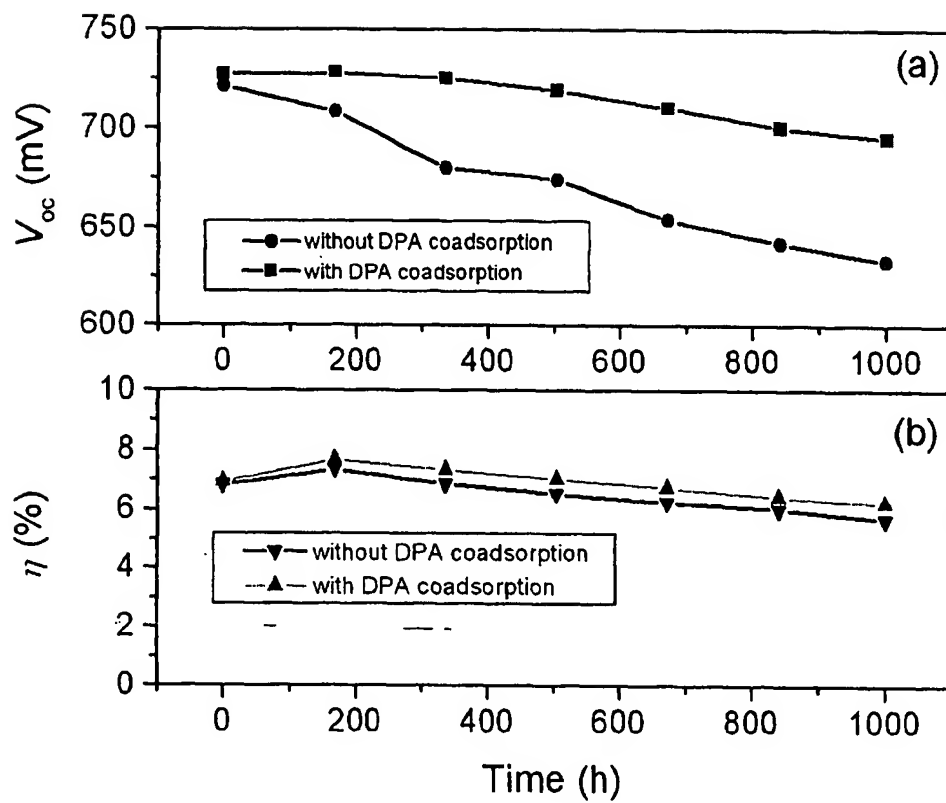


Figure 5





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 03 40 5306

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCl.7)
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Y	* the whole document *	3,5,6	
Y	BARBE C J ET AL: "nanocrystalline titanium oxide electrodes for photovoltaic applications" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, AMERICAN CERAMIC SOCIETY, COLUMBUS, US, vol. 80, no. 12, 1997, pages 3157-3171, XP002178698 ISSN: 0002-7820 * the whole document *	3,5,6	
A	DE VRIES J G ET AL: "Negative Ames-test of cis-di(thiocyanato)-N,N'-bis(4,4'-dicarboxy-2,2'-bipyridine)Ru(II), the sensitizer dye of the nanocrystalline TiO2 solar cell" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 60, no. 1, 1 January 2000 (2000-01-01), pages 43-49, XP004244716 ISSN: 0927-0248 * the whole document *	1-18	TECHNICAL FIELDS SEARCHED (InCl.7) H01G H01L
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The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>24 November 2003</b>	Examiner <b>Boero, M</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ..... &amp;: member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/02 (P04C01)

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24-11-2003

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